Chapter

Determination of Concentration for Some Priority Substances in Paddy Fields of Ergene River, Meriç River, and Yenikarpuzlu Dam, Turkey

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Abstract

This study was intended in paddy (rice husk and rice), sediment, and irrigation water samples taken from the paddy fields of Ergene River, Meriç River, and Yenikarpuzlu Dam reservoir which are frequently grown in the river basin in Thrace region and endosulfan (EN) and PAHs were investigated. For analysis, EN and PAHs were studied by GC-MS. The data obtained as a result of the analyses were compared with the results of the standard reference items, and the accuracy of the results was determined. The standard addition method was used to prove the accuracy of EN and PAHs. The recovery parameters on the extraction efficiency of EN and PAHs were optimized, and the recoveries ranged from 82 to 105%. The methods showed good linearity for EN and PAHs, and the LOD and LOQ for methods were found 0.03–63.1 and 0.1–210 μg kg^{-1}, respectively.

Keywords: Thrace region, paddy, sediment, water, endosulfan, PAHs

1. Introduction

Industrial and agricultural activities along with increasing industrialization are polluted very quickly of water and soil resources. When these sources of pollution are taken into consideration, it is necessary to follow the industrial and agricultural residues. These pollutants, which are used in agriculture and industry, interfere with the natural environment and threaten the ecological environment. Some pollutants can be found in the environment even after years of prohibition, and others can be transported over long distances. Pollutants are spread to the environment as industrial, agricultural and domestic sources [1, 2].

Direct transport of pesticides on the soil surface or on the plant play a role factors such as evaporation, surface flow, soil penetration and adsorption. Evaporation is on the soil, water and plant surface and the most important factor affecting the evaporation of pesticide is its evaporation pressure. In addition, high temperature, low relative humidity and air movement are environmental factors that accelerate evaporation. Pesticides strongly absorbed by soil particles are much less likely to evaporate [3–5].

Endosulfan (EN) is an organochlorine and acaricide group. Acute toxicity is a colorless, solid agricultural chemical prohibited due to its bioaccumulative potential

and endocrine disrupting effects [4–6]. EN residues in nature are also known to remain in the soil for at least 6 years [7, 8]. Therefore, it requires examination of the soil contaminated with EN, the product grown in soil, sediment and the water used. Polycyclic systems occur when one ring is sharing two carbons with another ring, or the rings are connected to each other by a C–C bond [9]. PAHs are from the group of compounds which show unsaturation in molecular formulas and do not give addition reactions which are characteristic for them. In the cyclic structure, PAHs from the class of planar molecules are resistant to oxidation. In addition, PAHs can be found in petrochemical, rubber, plastic, mineral oil, rust oil, paint, leather and other products. Rubber and plastic materials are high-risk materials containing PAH. In the Ergene Basin, where the industry is intense, these compounds are likely to be found. As the molecular weights of PAHs increase, their solubility in water decreases. However, their toxic and carcinogenic properties increase [9–12]. Contaminated soil, air and aquatic products may also contain PAH. The cooking meat or other food on the grill or at high temperatures increases the amount of PAH in food [11]. In this study, analysis of EN and PAHs compounds shown in **Figure 1** was performed.

The organic components (PAHs and EN) we analyzed are considered among the primary pollutants [9, 13–17]. When the pesticides in our ecological environment are taken in high concentration, they can cause deformations on the biological structure of the organism. In the event of prolonged exposure to certain pesticides, cancer can be seen or short-term exposure may result in direct death [13, 15–19].

The extensively used high sensitivity analytical techniques for the determination of EN and PAHs at low concentrations in environmental samples are

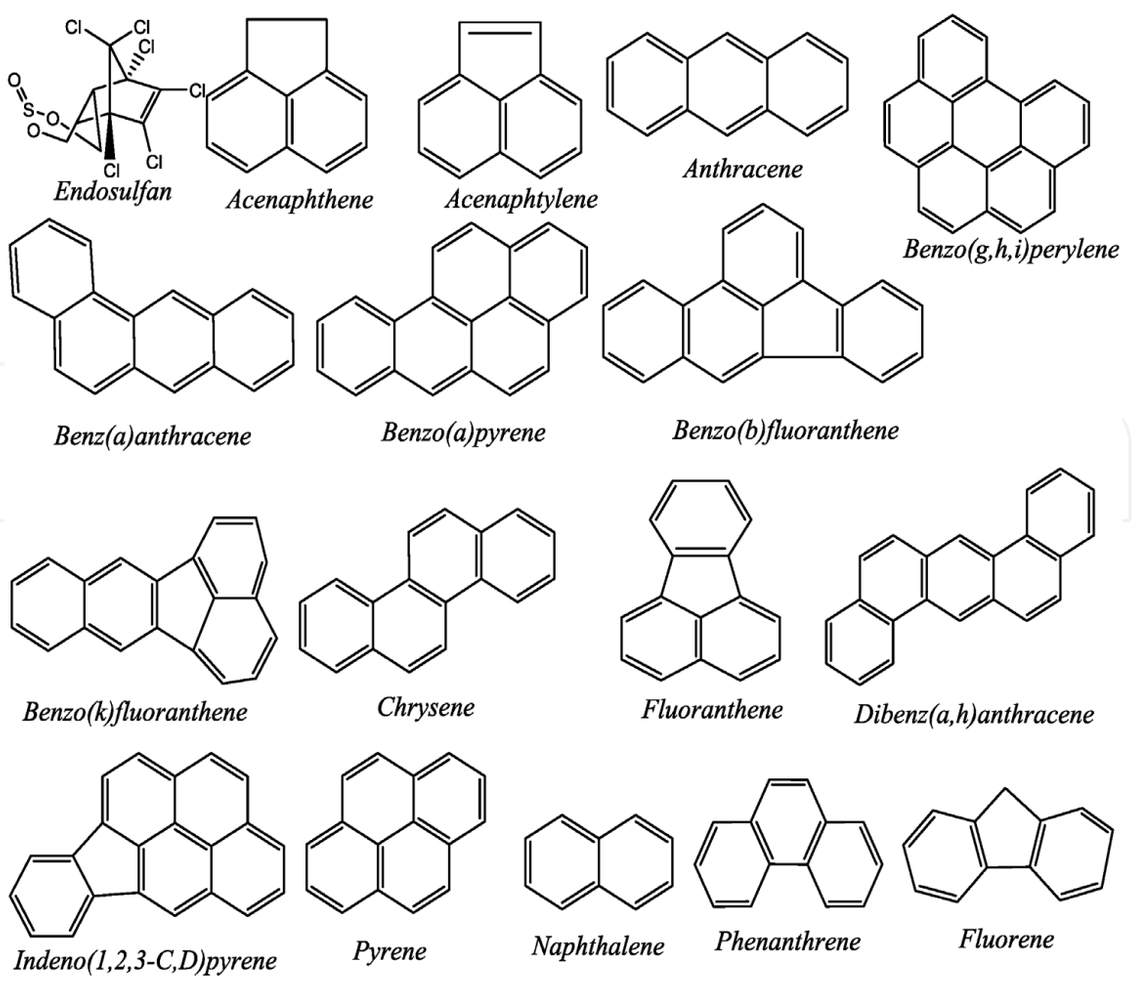

Figure 1.
Structural formulas of analyzed compounds.

GC-MS [6, 8, 20, 21], HPLC-MS [10, 22]. The separation and preconcentration techniques for pesticides are solid phase extraction (SPE) [21, 23, 24], solid phase micro extraction (SPME) [21, 22, 25] and sonication [22, 26], which are used to solve these problems in analysis of EN and PAHs.

The aim of this study was intended in paddy (rice husk and rice), sediment, and irrigation water samples taken from the paddy fields of Ergene River, Meriç River, and Yenikarpuzlu Dam reservoir which are frequently grown in the river basin in Thrace region and EN and PAHs were investigated. Thrace region is a place where industry and agriculture are intense, so the analysis with real examples will be performed of great importance here. For this reason, EN and PAHs, which developed method validation, were studied by GC-MS.

2. Materials and methods

Within the scope of this study, the paddy production areas in the agricultural areas of Thrace Region, direct irrigation from Ergene-Meriç rivers and dam ponds, Ergene and Meriç Basin were evaluated and three regions were determined as the study area. The sampling points are shown in **Figure 2**. Endosulfan and PAH analyses were made in paddy plant, sediment and irrigation water samples taken from paddy fields, which irrigated from the Ergene River, the Meriç River, and the Yenikarpuzlu Dam Reservoir, considering the distinction of irrigation resources in the rice plants often grown in river basins in the Thrace region. In the Yenikarpuzlu village of Edirne province, around Sığırcı Dam, and from the irrigated area from Edirne-İpsala-Yenikarpuzlu, Edirne-Merkez-Üyüklütatar and Edirne-Uzunköprü-Muhacirkadı Village were collected the paddy, sediment and paddy irrigation water (**Figure 2**). Endosulfan and PAH analysis were performed method validation by GC-MS.

Agilent GC-MS was used in the determination phase for all studies. The instrument used is the HP-5 MS UI capillary column (30 m × 250μm × 0.25 μm) and the 5990C (Agilent) inert MSD mass detector with 7890A (Agilent) model GC-MS. The electron ionization (EI) system with 70 eV ionization energy in GC-MS, and the He gas was used as carrier gas.

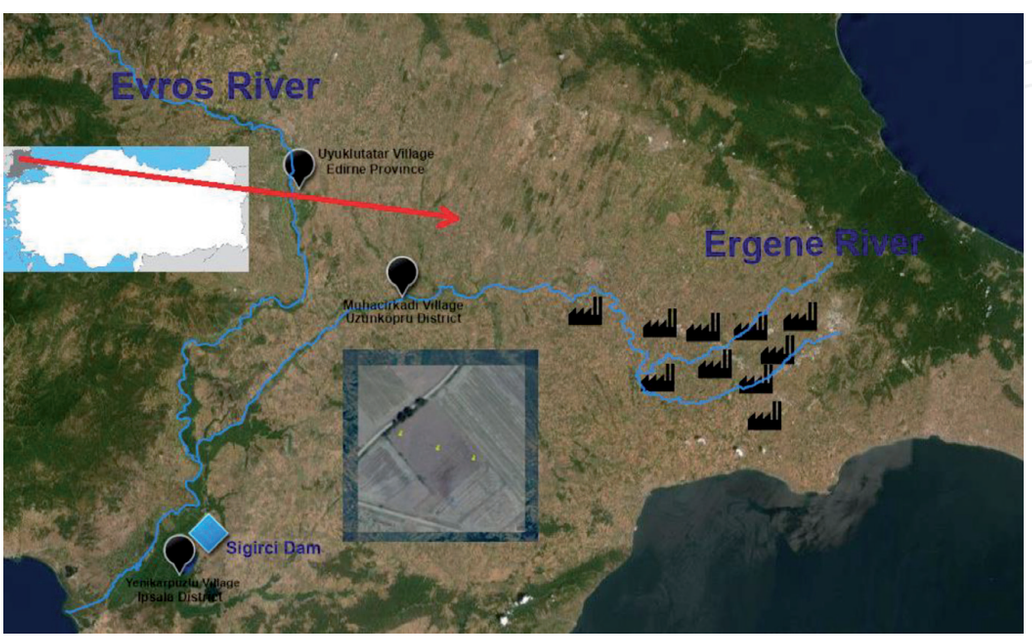

Figure 2.
Representation of the sampling points on the map.

2.1 Preparation of standard solutions

Dilution for Endosulfan (EN) was carried out on pure standard (SIGMA-ALDRICH, Product: 45852, EN solution 100 ng μL^{-1} in n-hexane, PESTANAL®). As a standard for PAHs, Dr. Ehrenstorfer 2095009 product PAH-mix 9 was used. In the standard, there are mixtures of 16 polycyclic aromatic hydrocarbons (PAHs); naphthalene (NAP), acenaphthalene (ACE), acenaphtylene (ACY), fluorene (FLU), phenantherene (PHN), anthracene (ANT), fluoranthene (FLR), pyrene (PYR), benz(a)anthracene (BaA), chrysene (CRY), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), dibenz(a,h)anthracene (DahA), benzo(g,h,i)perylene (BghiP) and indeno(1,2,3,c,d)pyrene (IcdP). Optimum conditions of EN and PAHs were shown in **Tables 1** and **2**. According to the mass spectra of the chromatograms of the EN and PAH pesticides, column retention times and ion inputs were studied in SIM mode. Pesticide standards were prepared (0.1, 0.25, 0.5, 1, 2, 2.5, 5, 7.5, 10, 25, 50, 100, 250, 500, 750 and 1000 $\mu g\ L^{-1}$) and measurements were taken. PAH-mix 9 of 16 polycyclic aromatic hydrocarbon compounds in standard contented NAP, ACE, ACY, FLU, PHN, ANT, FLR, PYR, BaA, CRY, BbF, BkF, BaP, DahA, BghiP and IcdP, and the dilution made out of from standard mixture was prepared standards of 1, 5, 10, and 25 $\mu g\ L^{-1}$. The methods applied in GC–MS for EN and PAHs are given in **Tables 1** and **2**, respectively.

The retention times (RT), SIM fragmentation ions, chromatogram programming times of PAHs are given in **Table 3**. The TICs of EN and PAHs were shown in **Figures 3** and **4**.

GC injection conditions				
Applied method			Splitless	
Injection volume			1 μL	
Temperature			250°C	
He gas flow rate			1 mL/min	
Total flow rate			64 mL/min	
Septum cleaning flow			3 mL/min	
Temperature program			250°C for 1 min	
Cleaning flow for split vent			60 mL/min throughout 2.5 min	
Transfer line temperature program			150°C for 0 min, runtime 30 min 280°C for 0 min, runtime 30 min	
Column oven temperature program			**MS information**	
			Collection mode	**Scan**
Rate (°C/min)	Temperature (°C)	Standby time (min)	Solvent delay (min)	10.00
			Gain factor	5.00
	45 (initial)	1	EM voltage obtained	2271
21	150	5	MS source temperature (°C)	230
4	220	0	MS Quad (°C)	150
	300 (post run)	3	Scanned mass range	100–279

Table 1.
The optimum GC-MS conditions applied for endosulfan.

GC injection conditions				
Applied method			Splitless	
Injection volume			1 μL	
Inlet temperature			70°C	
He gas flow rate			1 mL/min	
Total flow rate			64 mL/min	
Septum cleaning flow			3 mL/min	
Temperature program			300 °C for 1 min	
Cleaning flow for split vent			60 mL/min throughout 2.0 min	
Transfer line temperature program			150°C for 0 min, runtime 42.43 min 280°C for 0 min, runtime 41.43 min	
Column oven temperature program			**MS information**	
			Collection mode	**Scan**
Rate (°C/min)	Temperature (°C)	Standby time (min)	Solvent delay (min)	0.00
			Gain factor	5.00
	70 (initial)	1	EM voltage obtained	2329
10	120	1	MS source temperature (°C)	230
7	270	13	MS Quad (°C)	150
	300 (post run)	3	Scanned mass range	100–279

Table 2.
Optimum GC-MS conditions for PAHs.

Pesticides	**RT (min)**	**Target ion**	**Ion 1**	**Ion 2**	**Programming time (min)**
Naphthalene (NAP)	7.584	128.00	129.00	—	6.00
Acenaphthalene (ACE)	12.394	152.00	153.00	—	8.00
Acenaphtylene (ACY)	13.017	153.00	154.00	—	12.67
Fluorene (FLU)	14.694	166.00	165.00	—	13.50
Phenantherene (PHN)	17.846	178.00	176.00	179.00	15.00
Anthracene (ANT)	17.994	178.00	176.00	179.00	17.91
Fluoranthene (FLR)	21.850	202.00	200.00	203.00	18.10
Pyrene (PYR)	22.556	202.00	200.00	203.00	22.15
Benz(a)anthracene (BaA)	26.650	228.00	226.00	229.00	23.00
Chrysene (CRY)	26.879	228.00	226.00	229.00	26.71
Benzo(b)fluoranthene (BbF)	30.281	252.00	250.00	253.00	26.90
Benzo(k)fluoranthene (BkF)	30.376	252.00	250.00	253.00	30.33
Benzo(a)pyrene (BaP)	37.713	252.00	250.00	253.00	35.65
Benzo(g,h,i)perylene (BghiP)	31.539	276.00	138.00	277.00	31.70
Dibenz(a,h)anthracene (DahA)	38.082	276.00	278.00	279.00	37.95
Indeno(1,2,3,c,d)pyrene (IcdP)	39.436	276.00	274.00	277.00	38.50

Table 3.
The retention times (RT), SIM fragmentation ions, and chromatogram programming times of PAHs.

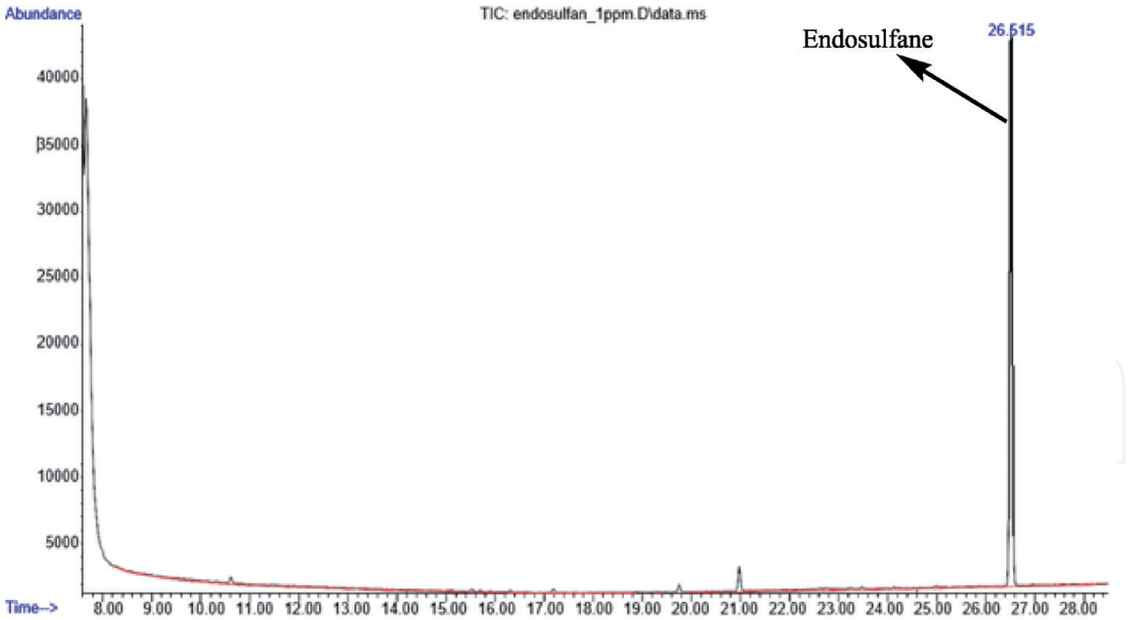

Figure 3.
GC chromatograms of Endosulfan compound.

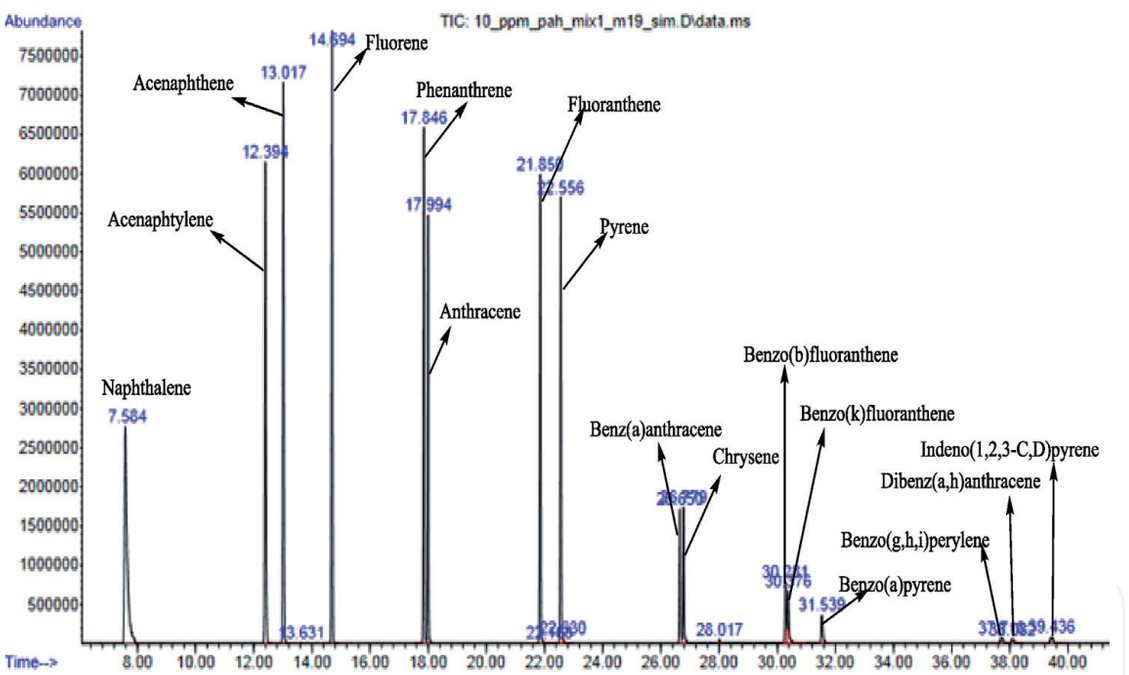

Figure 4.
GC chromatograms of PAH compounds.

The standards (EN and PAHs) were prepared in certain concentrations and readings were made in the device and the calibration graphs were plotted to calculate the amounts in the actual samples (**Figures 5** and **6**).

The linear regression, correlation coefficient, the detection limit (LOD) indicating the performance of the method in the method validation [14], the determination limit (LOQ), relative standard deviation percentage (RSD) and recovery calculations of the pesticides analyzed by GC-MS were shown in **Table 4**.

2.2 Collection of samples and preparation for analysis

For each point determined, twice samples were sampled in the months of July (sowing period) and September (harvesting period) in the periods of paddy sowing

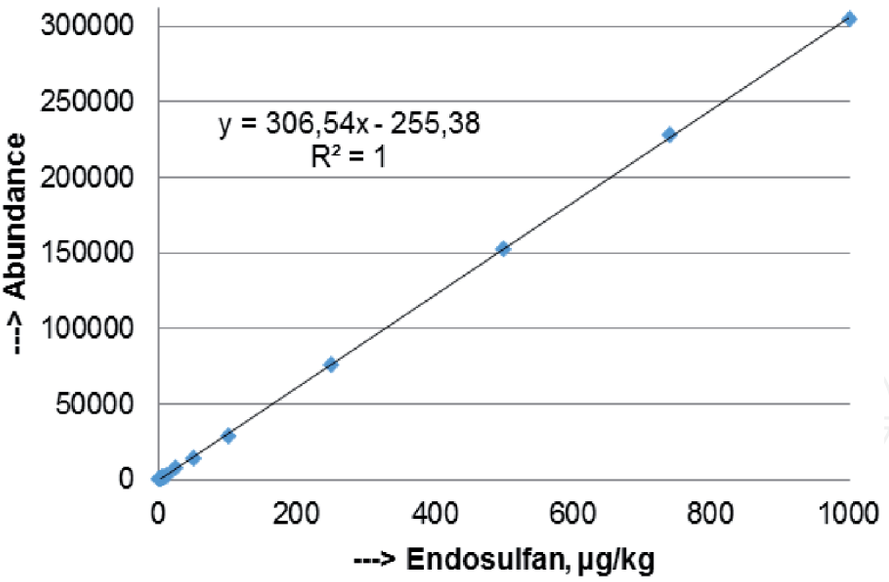

Figure 5.
The calibration graph of Endosulfan compound.

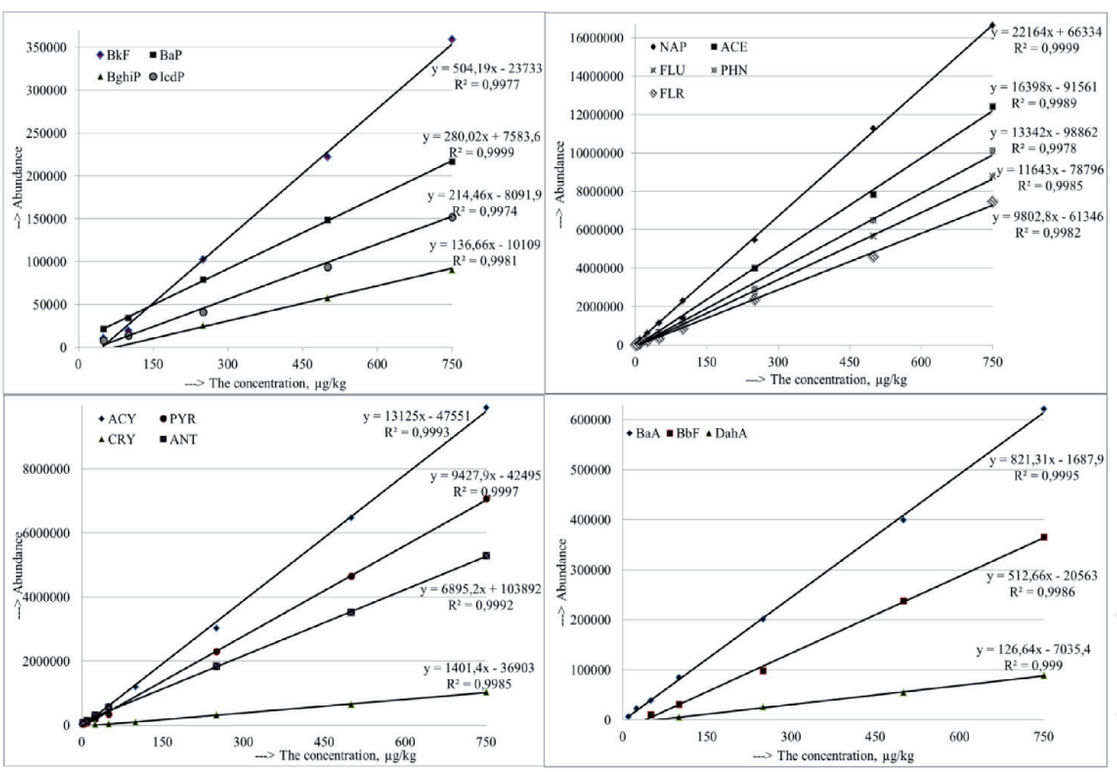

Figure 6.
The calibration graphs of PAHs compounds.

and harvesting. In the paddy pan, selected for sampling, three points were determined to represent each of the ceilings and pan water, soil and plant samples were made from these points. Since there were no paddy in the sowing period, only in the harvesting period of soil and water "at the latest 5 days before the harvest" were done every triple sampling. The pan water, sediment samples, rice grains and rice husk samples from the paddy samples were coded with the abbreviation "w," "sd," "r," and "rh," respectively. The coordinates of the locations, code and sampling dates are given in **Table 5**.

Water samples prepared for analysis of EN and PAHs are enriched in the solid phase extraction system and prepared for analysis by GC-MS. Plant and sediment

	Pesticides	Regression equation (linear range)	R^2	LOD	LOQ	RSD%	Recovery,%
1	EN	305.77x – 245.32 (1–1000 μg/kg)	0.9999	0.79	2.64	7.39	103
2	NAP	23,096x – 6571.3 (0.25–1000 μg/kg)	0.9984	0.03	0.10	1.85	105
3	ACE	16,398x – 91,561 (1–750 μg/kg)	0.9989	0.23	0.76	1.17	98.9
4	ACY	13,125x – 47,551 (0.5–750 μg/kg)	0.9993	0.05	0.17	0.42	101
5	FLU	11,643x – 78,796 (2.5–750 μg/kg)	0.9985	0.43	1.46	1.62	88.1
6	PHN	13,342x – 98,862 (2.5–750 μg/kg)	0.9978	0.64	2.12	2.17	96.5
7	ANT	6895.2x + 103,892 (2.5–750 μg/kg)	0.9992	1.17	3.89	3.65	100
8	FLR	9819.7x – 70,254 (2.5–750 μg/kg)	0.9981	0.64	2.12	2.28	91.6
9	PYR	9427.9x – 42,495 (2.5–750 μg/kg)	0.9997	0.67	2.24	3.42	97.6
10	BaA	821.31x – 1687.9 (25–750 μg/kg)	0.9995	4.05	13.52	4.96	92.9
11	CRY	1401.4x – 36,903 (25–750 μg/kg)	0.9985	6.78	22.6	1.35	86.9
12	BbF	512.66x – 20,563 (50–750 μg/kg)	0.9986	12.3	40.9	4.86	83.2
13	BkF	504.19x – 23,733 (50–750 μg/kg)	0.9977	17.4	58.1	6.8	84.3
14	BaP	280.02x + 7583.6 (100–1000 μg/kg)	0.9999	20.0	66.3	7.87	82.5
15	IcdP	136.66x – 10,109 (250–1000 μg/kg)	0.9981	63.1	210	3.33	86.1
16	NAP	127.67x – 7342 (250–1000 μg/kg)	0.9991	42.2	141	5.05	90.2
17	ACE	214.46x – 8091.9 (50–1000 μg/kg)	0.9974	14.0	46.7	5.72	95.0

Table 4.
The values of linear regression ($y = ax + b$), correlation coefficient (R^2), LOD (μg/kg), LOQ (μg/kg), and RSD% in the pesticides.

Coordinates	Sowing period			Harvest period		
	Code	Sampling date	Watering source	Code	Sampling date	Watering source
40°48′25.0″N 26°18′58.9″E	**1-w**	20.07.2016	Dam Lake	**11-w**	22.09.2016	Dam Lake
				11-sd		
	1-sd			**11-r**		
				11-rh		
41°32′19.7″N 26°36′14.4″E	**2-w**	27.07.2016	Meriç River	**22-w**	23.09.2016	Meriç River
				22-sd		
	2-sd			**22-r**		
				22-rh		
41°20′17.8″N 26°52′31.6″E	**3-w**	02.08.2016	Ergene River	**33-w**	21.09.2016	Ergene River
				33-sd		
	3-sd			**33-r**		
				33-rh		

Table 5.
Sampling's coordinates, codes, and dates.

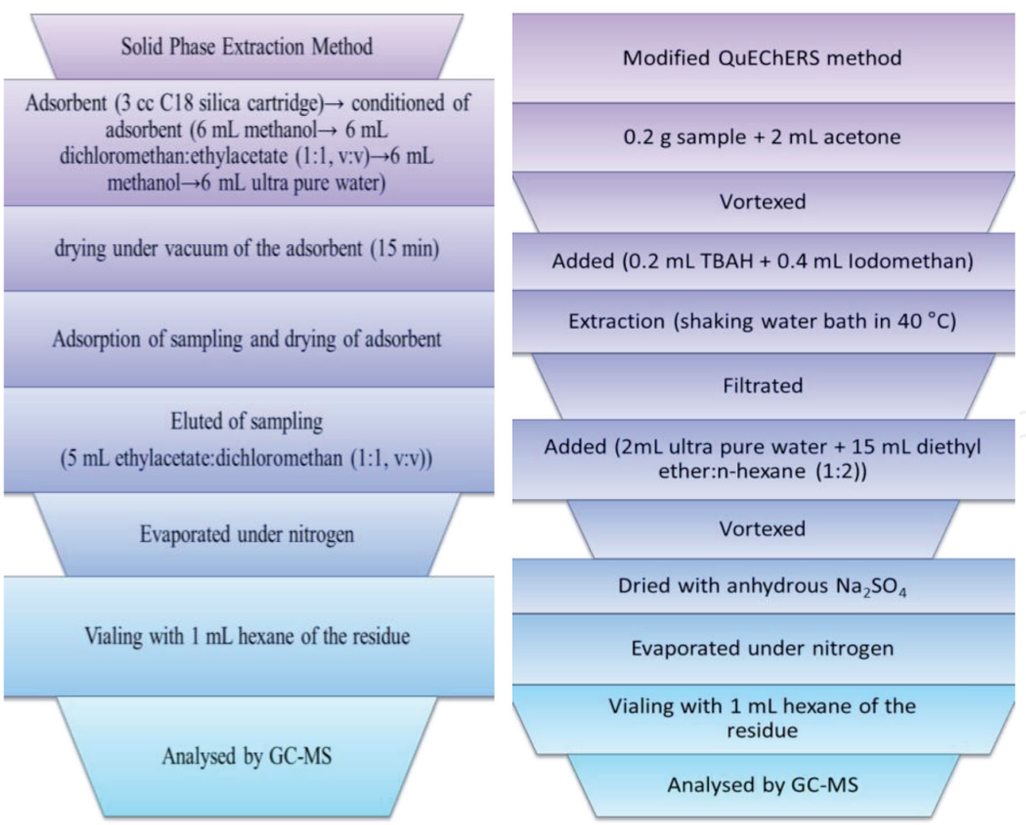

Figure 7.
The enrichment of samples with the solid phase extraction and modified QuEChERS methods.

samples were enriched with modified QuEChERS method and prepared for analysis by GC-MS. The contents of the solid phase extraction and modified QuEChERS methods are given in **Figure 7**.

3. Results and discussion

Along with the developments in industrialization, it has made it necessary to determine organo-contaminant at major and minor levels in the settlements where there is a large amount of factories. In this study, The analysis of EN, NAP, ACE, ACY, FLU, PHN, ANT, FLR, PYR, BaA, CRY, BbF, BkF, BaP, DahA, BghiP and IcdP were performed in paddy, sediment and water samples taken during paddy planting and harvesting from the places such as Yeni Karpuzlu Dam, Muhacirkadı Village (Ergene River) and Üyüklütatar Village (Meriç River). These analyses were performed by using GC-MS. The results of the analysis of EN and PAHs in samples were given in **Tables 6**-**8**.

Large scale accumulation or pollution of pesticide chemicals or natural chemicals is a source of concern for our global world. Due to the incorporation of these substances into the condensation and evaporation cycle, our natural life creates constant exposure with rain, snow and fog [26]. Soil pollution is closely related to industrial activities, destruction of municipal and industrial waste or environmental accidents. Soil is a complex and heterogeneous matrix with a porous structure containing inorganic and natural organic components [1, 2].

PAH components, which come out from the chemical production factories and vehicles' exhausts along the Ergene River, constitute a serious source of pollution. In the Ergene Basin is located in petrochemical, rubber, plastic, mineral oil, rust oil, paint, leather and other products. Rubber and plastic materials including PAHs are high-risk materials. For this reason, EN and PAHs analyses of the samples collected from rice cultivated areas in the basin selected as clean region (Yeni Karpuzlu Dam), dirty region (Muhacirkadı Village) and less dirty region (Üyüklütatar Village) were determined. As the molecular weights of PAHs increase, their solubility in water decreases and accumulation in the sediment also increases. When the results obtained are examined, it can be seen that PAHs accumulate in the sediment.

Sampling during the sowing period and harvest period were made classifications as for proximity to the road, and irrigation channel, or proximity to the dam with code of 1B-1 and 11B-1, intermediate zones of 1B-2 and 11B-2, and the more distant area of 1B-3 and 11B-3.

The recoveries for EN and PAHs were ranged from 82.5 to 105%, respectively. The LOD and LOQ for EN and PAHs were found 0.03–63.1 and 0.1–210 μg kg^{-1}, respectively.

The amount of EN, NP, ACE, ACY, FLU, PHN, ANT, FLR, PYR, BaA, CRY, BbF, BkF, BaP and IcdP in sediment samples were found to be 17.5–44.9 mg kg^{-1}, 219–417 μg kg^{-1}, 41.1–64.1 μg kg^{-1}, 176–264 μg kg^{-1}, Nd–70.5 μg kg^{-1}, 66.7–318 μg kg^{-1}, 20.3–485 μg kg^{-1}, 137–273 μg kg^{-1}, 790–1867 μg kg^{-1}, 113–1549 μg kg^{-1}, Nd–1190 μg kg^{-1}, Nd–1775 μg kg^{-1}g, Nd–1436 μg kg^{-1}, Nd–2478 μg kg^{-1} and Nd–968 μg kg^{-1}, respectively. The pesticide concentrations of BghiP and DahA in sediment samples were found below the limit of determination.

The amount of EN, NP, ACE, ACY, FLU, PHN, ANT, FLR, PYR, BaA, and CRY in water samples were found to be Nd–11.1 mg L^{-1}, 38.3–105 μg L^{-1}, Nd–10.3 μg L^{-1}, 8.30–14.8 μg L^{-1}, 6.73–10.6 μg L^{-1}, 44.8–104 μg L^{-1}, 18.7–152 μg L^{-1}, 16.2–65.4 μg L^{-1}, 45.0–92.4 μg L^{-1}, 19.4–88.3 μg $L^{-1}$and Nd–85.4 μg L^{-1}, respectively. The sample chromatograms of EN and PAHs in sediment, water, rice and rice husk are shown in **Figures 8** and **9**. Except for the clean area, EN was determined above the limit of detection in other sampling areas. The amount of EN in the dirty area was determined as ND-11.1 μg L^{-1}. In the Harvest period for the polluted region were found 7.85, 7.99, and 8.64 μg L^{-1}, respectively.

		Sowing period			Harvest period		
		1Bsd1	**1Bsd2**	**1Bsd3**	**11Bsd1**	**11Bsd2**	**11Bsd3**
Dam Basin	EN, mg/kg	31.7 ± 1.7	28.0 ± 2.5	21.8 ± 2.6	17.5 ± 1.3	29.0 ± 2.3	22.5 ± 1.2
	NAP, μg/kg	385 ± 30	376 ± 2	325 ± 5	306 ± 8	307 ± 24	314 ± 26
	ACE, μg/kg	61.8 ± 2.6	63.7 ± 5.6	62.5 ± 1.9	59.7 ± 4.1	54.7 ± 5.3	53.0 ± 4.6
	ACY, μg/kg	264 ± 1	254 ± 14	226 ± 9	208 ± 7	223 ± 10	212 ± 16
	FLU, μg/kg	55.6 ± 1.5	70.5 ± 2.9	47.8 ± 2.8	45.1 ± 3.8	53.9 ± 1.3	66.7 ± 2.9
	PHN, μg/kg	318 ± 18	263 ± 23	164 ± 13	124 ± 8	113 ± 3	120 ± 5
	ANT, μg/kg	485 ± 34	383 ± 35	197 ± 2	122 ± 11	102 ± 6	115 ± 8
	FLR, μg/kg	273 ± 10	247 ± 15	236 ± 2	201 ± 14	204 ± 13	204 ± 10
	PYR, μg/kg	1867 ± 126	1617 ± 54	1622 ± 55	1265 ± 99	1245 ± 54	1291 ± 48
	BaA, μg/kg	708 ± 70	1231 ± 110	1244 ± 95	424 ± 42	497 ± 36	113 ± 7
	CRY, μg/kg	1058 ± 75	1190 ± 32	Nd	Nd	Nd	Nd
	BbF, μg/kg	970 ± 57	1775 ± 34	Nd	1293 ± 51	1074 ± 48	1118 ± 30
	BkF, μg/kg	1359 ± 112	1436 ± 47	900 ± 91	1354 ± 44	1124 ± 49	1163 ± 102
	BaP, μg/kg	2462 ± 159	1768 ± 14	2478 ± 121	383 ± 38	1737 ± 119	312 ± 31
	IcdP, μg/kg	867 ± 3	968 ± 59	846 ± 42	921 ± 19	758 ± 53	815 ± 58

		Sowing period			Harvest period		
Meriç-Üyüklütatar Village		**2Bsd1**	**2Bsd2**	**2Bsd3**	**22Bsd1**	**22Bsd2**	**22Bsd3**
	EN, mg/kg	27.0 ± 1.7	24.2 ± 1.9	29.9 ± 2.4	36.9 ± 3.6	44.9 ± 2.7	39.7 ± 2.3
	NAP, µg/kg	336 ± 22	278 ± 18	321 ± 14	296 ± 12	311 ± 33	254 ± 24
	ACE, µg/kg	64.1 ± 1.2	58.5 ± 4.6	58.5 ± 5.1	55.3 ± 4.9	54.6 ± 3.9	50.4 ± 3.1
	ACY, µg/kg	248 ± 17	208 ± 16	244 ± 10	249 ± 28	233 ± 5	258 ± 15
	FLU, µg/kg	44.6 ± 4.4	44.0 ± 1.9	43.8 ± 3.4	50.3 ± 1.1	39.6 ± 3.9	38.9 ± 0.1
	PHN, µg/kg	104 ± 9	126 ± 5	104 ± 12	108 ± 1	69.2 ± 6.1	77.4 ± 3.7
	ANT, µg/kg	85.5 ± 3.1	127 ± 9	67.9 ± 5.2	93.7 ± 1.2	21.0 ± 1.3	36.3 ± 3.5
	FLR, µg/kg	212 ± 1	212 ± 13	196 ± 13	182 ± 5	156 ± 12	149 ± 11
	PYR, µg/kg	1407 ± 61	1415 ± 109	1328 ± 107	1160 ± 17	969 ± 92	881 ± 71
	BaA, µg/kg	1115 ± 108	519 ± 7	341 ± 33	749 ± 53	1093 ± 67	154 ± 15
	CRY, µg/kg	1136 ± 120	Nd	Nd	Nd	777 ± 69	Nd
	BbF, µg/kg	1171 ± 112	1084 ± 99	885 ± 53	1122 ± 109	753 ± 64	661 ± 52
	BkF, µg/kg	1427 ± 123	1011 ± 37	368 ± 16	1391 ± 22	801 ± 67	Nd
	BaP, µg/kg	136 ± 17	Nd	310 ± 25	160 ± 14	Nd	Nd
	IcdP, µg/kg	797 ± 36	777 ± 49	768 ± 95	692 ± 8	Nd	Nd
	IcdP, µg/kg	797 ± 36	777 ± 49	768 ± 95	692 ± 8	Nd	Nd

		Sowing period			Harvest period		
Muhacirkadı-Ergene Basin		**3Bsd1**	**3Bsd2**	**3Bsd3**	**33Bsd1**	**33Bsd2**	**33Bsd3**
	EN, mg/kg	21.4 ± 2.2	23.0 ± 1.6	26.5 ± 1.9	33.7 ± 2.5	21.7 ± 2.3	23.3 ± 2.3
	NAP, μg/kg	322 ± 12	417 ± 21	408 ± 18	219 ± 19	242 ± 23	226 ± 18
	ACE, μg/kg	56.5 ± 3.6	61.5 ± 1.2	56.8 ± 2.6	51.9 ± 2.0	44.1 ± 1.8	57.5 ± 3.4
	ACY, μg/kg	232 ± 18	258 ± 12	237 ± 7	235 ± 14	197 ± 19	176 ± 16
	FLU, μg/kg	44.6 ± 0.7	48.6 ± 3.8	46.0 ± 1.4	Nd	62.4 ± 2.5	50.7 ± 4.1
	PHN, μg/kg	102 ± 6	113 ± 5	77.8 ± 4.7	68.9 ± 6.4	66.7 ± 2.8	101 ± 3
	ANT, μg/kg	81.7 ± 6.4	103 ± 9	99.3 ± 2.5	20.3 ± 1.1	27.9 ± 2.1	79.6 ± 6.2
	FLR, μg/kg	190 ± 1	137 ± 4	196 ± 14	137 ± 7	245 ± 16	179 ± 5
	PYR, μg/kg	1275 ± 72	1314 ± 62	1279 ± 90	790 ± 78	1086 ± 47	1099 ± 52
	BaA, μg/kg	659 ± 66	771 ± 78	1549 ± 143	576 ± 41	664 ± 55	570 ± 50
	CRY, μg/kg	Nd	Nd	989 ± 91	674 ± 32	521 ± 23	Nd
	BbF, μg/kg	1194 ± 28	1014 ± 59	1047 ± 96	Nd	Nd	589 ± 36
	BkF, μg/kg	1243 ± 27	580 ± 12	1098 ± 37	Nd	577 ± 32	732 ± 33
	BaP, μg/kg	Nd	Nd	Nd	62.0 ± 6.2	483 ± 38	Nd
	IcdP, μg/kg	715 ± 28	728 ± 32	708 ± 24	Nd	Nd	Nd

Table 6.
Amount of pesticides in sediment samples in the dam basin, Meriç-Üyüklütatar village, and Muhacirkadı-Ergene Basin (n = 6).

		Sowing Period			Harvest Period		
		1Bw1	**1Bw2**	**1Bw3**	**11Bw1**	**11Bw2**	**11Bw3**
Dam Basin	EN, mg/kg	Nd	Nd	Nd	Nd	Nd	Nd
	NAP, µg/kg	47.6 ± 4.4	47.3 ± 3.4	58.9 ± 2.9	70.1 ± 0.1	47.2 ± 3.2	105 ± 9
	ACE, µg/kg	6.44 ± 0.05	10.3 ± 0.6	Nd	Nd	Nd	Nd
	ACY, µg/kg	8.66 ± 0.87	8.76 ± 0.21	9.68 ± 0.48	12.6 ± 0.7	10.3 ± 1.2	13.8 ± 1.1
	FLU, µg/kg	7.93 ± 0.78	6.73 ± 3.4	8.07 ± 0.27	6.76 ± 0.14	6.74 ± 0.37	7.70 ± 0.61
	PHN, µg/kg	60.6 ± 2.0	104 ± 6	70.4 ± 2.2	44.8 ± 6.1	52.7 ± 1.9	53.8 ± 3.5
	ANT, µg/kg	91.6 ± 3.8	18.7 ± 0.7	110 ± 4	62.0 ± 1.9	76.9 ± 3.6	79.0 ± 6.6
	FLR, µg/kg	18.2 ± 0.6	65.4 ± 4.2	18.3 ± 0.63	16.2 ± 1.6	17.5 ± 0.6	16.5 ± 0.8
	PYR, µg/kg	66.6 ± 4.1	45.0 ± 3.4	62.0 ± 3.1	58.5 ± 0.3	65.8 ± 5.3	55.7 ± 4.2
	BaA, µg/kg	45.5 ± 2.3	63.9 ± 3.2	39.6 ± 3.0	34.9 ± 3.4	38.4 ± 3.3	30.5 ± 1.9
	CRY, µg/kg	62.0 ± 4.3	Nd	Nd	Nd	60.8 ± 0.8	Nd
Meriç-Üyüklütatar Village		**2Bw1**	**2Bw2**	**2Bw3**	**22Bw1**	**22Bw2**	**22Bw3**
	EN, mg/kg	10.6 ± 0.3	Nd	Nd	Nd	Nd	Nd
	NAP, µg/kg	47.4 ± 1.1	53.7 ± 4.6	49.2 ± 2.5	39.5 ± 1.8	43.1 ± 2.2	41.1 ± 1.2
	ACE, µg/kg	Nd	Nd	6.60 ± 0.01	Nd	Nd	Nd
	ACY, µg/kg	8.86 ± 0.71	10.1 ± 0.8	7.86 ± 0.51	9.97 ± 0.13	8.30 ± 0.30	9.10 ± 1.9
	FLU, µg/kg	7.24 ± 0.31	8.26 ± 0.47	7.58 ± 0.72	7.41 ± 0.42	6.84 ± 0.26	7.12 ± 0.59
	PHN, µg/kg	71.0 ± 2.5	79.1 ± 5.8	69.1 ± 1.1	62.1 ± 4.2	60.8 ± 6.3	61.4 ± 5.3
	ANT, µg/kg	111 ± 5	126 ± 10	108 ± 2	94.5 ± 7.9	92.0 ± 7.5	93.3 ± 3.8
	FLR, µg/kg	18.4 ± 0.6	20.4 ± 1.2	20.0 ± 1.4	17.2 ± 0.4	16.9 ± 0.6	17.3 ± 1.2
	PYR, µg/kg	61.8 ± 2.1	71.8 ± 3.2	75.7 ± 6	51.8 ± 3.7	50.8 ± 3.2	54.1 ± 3.8
	BaA, µg/kg	39.3 ± 0.4	44.7 ± 1.9	59.9 ± 4.1	27.4 ± 2.6	26.1 ± 2.1	29.7 ± 2.3
	CRY, µg/kg	Nd	Nd	Nd	Nd	Nd	Nd

		Sowing Period			Harvest Period		
Muhacirkadı-Ergene Basin		**3Bw1**	**3Bw2**	**3Bw3**	**33Bw1**	**33Bw2**	**33Bw3**
	EN, mg/kg	11.1 ± 0.6	7.36 ± 0.63	Nd	8.64 ± 0.32	7.85 ± 0.81	7.99 ± 0.46
	NAP, μg/kg	73.5 ± 2.1	53.0 ± 2.7	58.3 ± 3.9	42.4 ± 1.8	38.3 ± 1.1	46.7 ± 4.5
	ACE, μg/kg	6.82 ± 0.19	Nd	Nd	Nd	Nd	Nd
	ACY, μg/kg	14.8 ± 1.4	14.6 ± 0.69	13.7 ± 1.3	12.7 ± 1.1	10.4 ± 0.8	12.8 ± 1.1
	FLU, μg/kg	10.6 ± 0.8	8.84 ± 0.12	9.09 ± 0.74	7.90 ± 0.58	7.41 ± 0.31	8.54 ± 0.52
	PHN, μg/kg	93.0 ± 1.4	83.3 ± 2.3	76.3 ± 6.2	76.3 ± 0.9	70.5 ± 6.1	88.4 ± 6.6
	ANT, μg/kg	152 ± 9	134 ± 4	121 ± 11	121 ± 2	110 ± 6	144 ± 12
	FLR, μg/kg	24.2 ± 1.5	20.6 ± 0.8	19.0 ± 0.7	18.7 ± 0.2	17.5 ± 1.0	16.9 ± 0.1
	PYR, μg/kg	92.4 ± 1.6	72.8 ± 5.3	63.0 ± 5.1	61.7 ± 1.6	53.7 ± 4.2	48.7 ± 0.4
	BaA, μg/kg	88.3 ± 5.2	43.1 ± 4.1	43.3 ± 2.4	33.3 ± 2.5	30.6 ± 0.9	19.4 ± 0.0
	CRY, μg/kg	85.4 ± 2.4	Nd	Nd	Nd	Nd	Nd

Table 7.
Amount of pesticides in water samples in in the dam basin, Meriç-Üyüklütatar village, and Muhacirkadı-Ergene Basin (n = 6).

		Rice Harvest Period			Rice Husk Harvest Period		
Dam Basın		**11Br1**	**11Br2**	**11Br3**	**11Brh1**	**11Brh2**	**11Brh3**
	EN, mg/kg	54.9 ± 4.6	46.4 ± 2.7	54.0 ± 2.8	47.4 ± 0.2	46.7 ± 1.6	41.6 ± 1.7
	NAP, µg/kg	220 ± 12	265 ± 18	280 ± 3	679 ± 27	420 ± 29	327 ± 6
	ACE, µg/kg	58.3 ± 0.4	55.3 ± 0.9	65.1 ± 2.3	246 ± 6	265 ± 16	239 ± 10
	ACY, µg/kg	205 ± 5	246 ± 7	216 ± 2	444 ± 3	374 ± 14	341 ± 6
	FLU, µg/kg	71.9 ± 2.8	76.7 ± 2.3	99.0 ± 4.3	62.3 ± 0.4	59.1 ± 0.3	75.2 ± 0.1
	PHN, µg/kg	204 ± 4	267 ± 7	192 ± 1	259 ± 18	145 ± 2	181 ± 10
	ANT, µg/kg	274 ± 7	396 ± 14	250 ± 2	416 ± 32	157 ± 9	324 ± 7
	FLR, µg/kg	179 ± 3	195 ± 1	194 ± 4	145 ± 4	185 ± 4	229 ± 2
	PYR, µg/kg	1068 ± 25	1148 ± 12	1142 ± 15	779 ± 20	1080 ± 19	1351 ± 21
	BaA, µg/kg	1614 ± 37	1871 ± 86	1770 ± 63	1900 ± 100	2100 ± 17	2760 ± 88
	CRY, µg/kg	1101 ± 22	1247 ± 59	1190 ± 30	1247 ± 59	1317 ± 18	1765 ± 58
	BbF, µg/kg	Nd	796 ± 79	226 ± 25	961 ± 91	945 ± 93	1303 ± 20
	BkF, µg/kg	Nd	Nd	254 ± 24	999 ± 99	1036 ± 103	1253 ± 8
	IcdP, µg/kg	1044 ± 73	1101 ± 24	843 ± 7	2076 ± 66	2134 ± 11	2343 ± 51

		Rice Harvest Period			Rice Husk Harvest Period		
Meriç-Üyüklütatar Village		**22Br1**	**22Br2**	**22Br3**	**22Brh1**	**22Brh2**	**22Brh3**
	EN, mg/kg	53.2 ± 1.4	60.1 ± 3.7	58.4 ± 1.6	43.4 ± 2.8	42.4 ± 3.5	41.8 ± 3.1
	NAP, μg/kg	239 ± 7	356 ± 29	383 ± 18	809 ± 23	628 ± 50	882 ± 25
	ACE, μg/kg	63.4 ± 0.9	70.5 ± 0.9	60.3 ± 1.5	179 ± 12	150 ± 3	153 ± 7
	ACY, μg/kg	194 ± 4	242 ± 7	275 ± 7	403 ± 10	401 ± 12	382 ± 16
	FLU, μg/kg	73.7 ± 3.3	51.0 ± 1.5	208 ± 15	105 ± 4	92.5 ± 3.1	102 ± 1
	PHN, μg/kg	79.3 ± 1.6	139 ± 7	428 ± 16	179 ± 1	193 ± 3	254 ± 5
	ANT, μg/kg	39.6 ± 2.9	172 ± 9	338 ± 26	52.1 ± 5.1	235 ± 6	402 ± 8
	FLR, μg/kg	195 ± 4	213 ± 4	228 ± 3	239 ± 8	297 ± 3	270 ± 7
	PYR, μg/kg	1176 ± 19	1196 ± 16	1349 ± 18	1436 ± 40	1916 ± 33	1673 ± 48
	BaA, μg/kg	1120 ± 52	1478 ± 71	1831 ± 101	2014 ± 79	3788 ± 141	3909 ± 180
	CRY, μg/kg	829 ± 25	969 ± 53	1225 ± 67	1330 ± 42	2375 ± 82	2400 ± 123
	BbF, μg/kg	215 ± 6	202 ± 3	617 ± 8	950 ± 94	294 ± 29	1261 ± 38
	BkF, μg/kg	245 ± 6	261 ± 5	270 ± 26	918 ± 85	537 ± 31	1120 ± 32
	IcdP, μg/kg	893 ± 6	948 ± 24	1395 ± 55	2637 ± 80	1426 ± 21	2058 ± 75

		Rice Harvest Period			Rice Husk Harvest Period		
Muhacirkadı-Ergene Basin		**33Br1**	**33Br2**	**33Br3**	**33Brh1**	**33Brh2**	**33Brh3**
	EN, mg/kg	50.2 ± 2.1	17.7 ± 0.5	28.4 ± 1.5	45.6 ± 1.2	47.2 ± 1.6	41.6 ± 3.2
	NAP, µg/kg	285 ± 5	445 ± 34	514 ± 42	603 ± 53	524 ± 36	517 ± 31
	ACE, µg/kg	77.0 ± 1.4	55.0 ± 0.2	59.9 ± 0.7	74.9 ± 2.7	94.4 ± 2.2	78.7 ± 4.0
	ACY, µg/kg	272 ± 8	331 ± 7	336 ± 23	364 ± 19	337 ± 9	313 ± 12
	FLU, µg/kg	250 ± 14	176 ± 4	294 ± 16	268 ± 25	168 ± 13	102 ± 3
	PHN, µg/kg	269 ± 22	518 ± 9	336 ± 30	197 ± 4	225 ± 5	189 ± 3
	ANT, µg/kg	392 ± 33	859 ± 18	519 ± 15	216 ± 2	199 ± 3	205 ± 8
	FLR, µg/kg	222 ± 6	191 ± 4	125 ± 6	358 ± 8	378 ± 7	358 ± 9
	PYR, µg/kg	1202 ± 30	1078 ± 32	789 ± 2	2293 ± 36	2576 ± 43	2336 ± 55
	BaA, µg/kg	1717 ± 6	1560 ± 67	895 ± 61	2415 ± 46	3766 ± 163	4258 ± 169
	CRY, µg/kg	1152 ± 10	1077 ± 37	752 ± 5	1526 ± 44	2413 ± 109	2562 ± 52
	BbF, µg/kg	901 ± 75	1029 ± 57	1255 ± 115	1256 ± 127	1042 ± 22	1220 ± 37
	BkF, µg/kg	949 ± 48	1403 ± 105	599 ± 22	1722 ± 134	1061 ± 31	929 ± 35
	IcdP, µg/kg	1397 ± 24	1531 ± 23	1392 ± 41	2332 ± 96	2300 ± 22	1988 ± 52

Table 8.
The amounts of pesticides in the samples of rice and rice husk in the dam basin, Meriç-Üyüklütatar village and Muhacirkadı-Ergene Basin (n = 6).

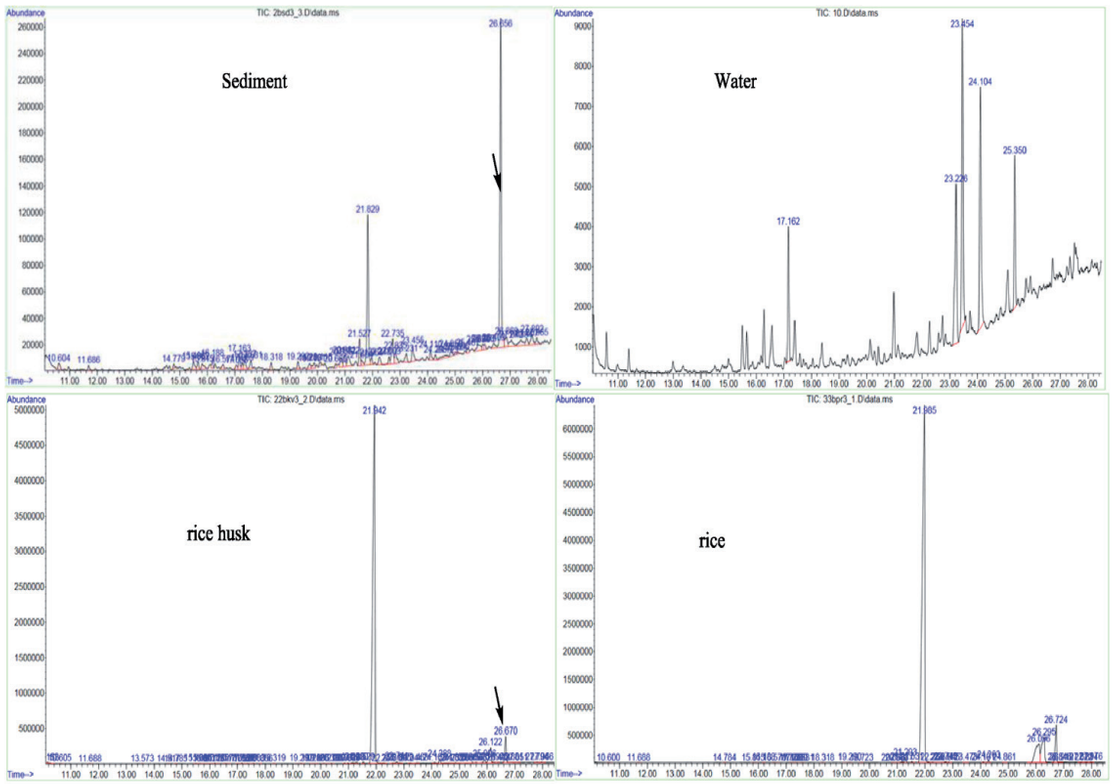

Figure 8.
Endosulfan chromatograms of samples taken from the paddy grown area.

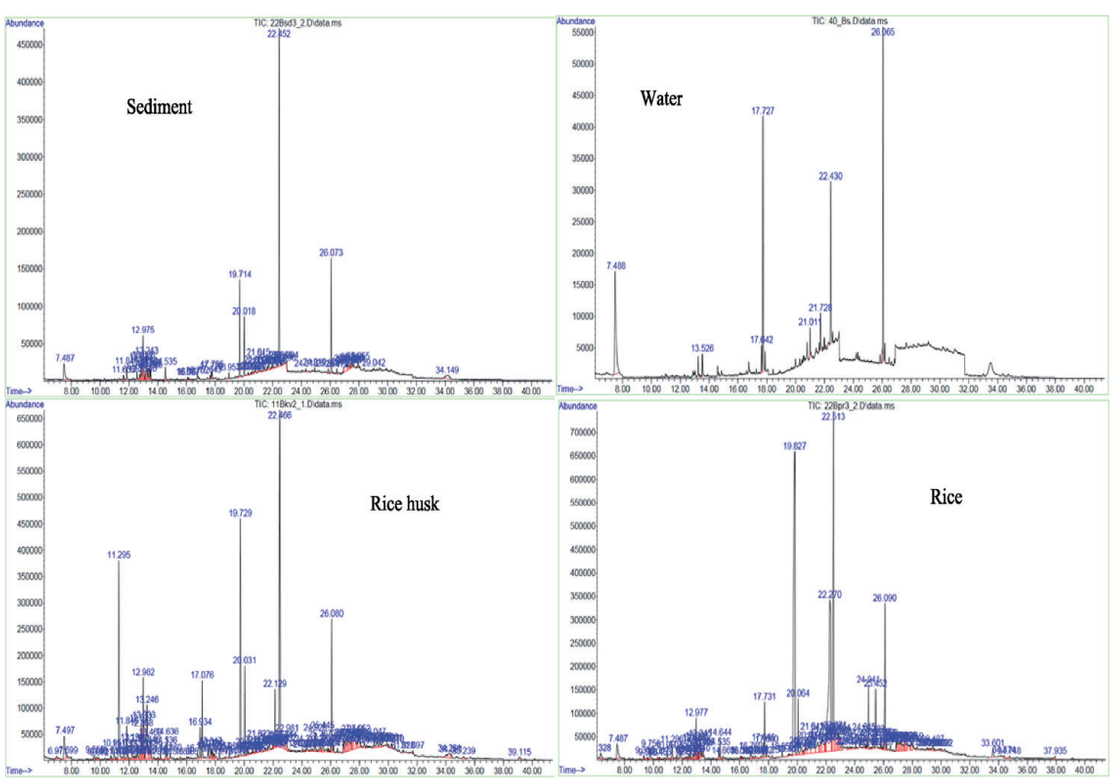

Figure 9.
PAH chromatogram of samples taken from the paddy grown area.

Pesticides strongly absorbed by soil particles are much less likely to evaporate [1, 2, 24]. Since pesticides are more adsorbed in sediment samples, their transition to water decreases. The results were confirmed this. Sodium was

found in higher concentrations than sediment samples because of its high solubility in water. This increases the electrical conductivity and reduces the water quality.

The amount of EN, NP, ACE, ACY, FLU, PHN, ANT, FLR, PYR, BaA, CRY, BbF, BkF and IcdP in rice samples were found to be 17.7–60.1 mg kg^{-1}, 220–514 μg kg^{-1}, 55.0–77.0 μg kg^{-1}, 194–336 μg kg^{-1}, 51.0–294 μg kg^{-1}, 79.3–518 μg kg^{-1}, 39.6–859 μg kg^{-1}, 125–228 μg kg^{-1}, 798–1349 μg kg^{-1}, 895–1871 μg kg^{-1}, 752–1247 μg kg^{-1}, Nd–1255 μg kg^{-1}, Nd–1403 μg kg^{-1} and 843–1531 μg kg^{-1}, respectively. The pesticide concentrations of BaP, BghiP, DahA in rice samples were found below the limit of determination. The amount of PAHs in the polluted region was more than twice that of the clean region.

The amount of EN, NAP, ACE, ACY, FLU, PHN, ANT, FLR, PYR, BaA, CRY, BbF, BkF and IcdP in the rice husk samples were found to be 41.6–46.7 mg kg^{-1}, 327–882 μg kg^{-1}, 74.9–265 μg kg^{-1}, 313–444 μg kg^{-1}, 59.1–268 μg kg^{-1}, 145–259 μg kg^{-1}, 52.1–416 μg kg^{-1}, 145–378 μg kg^{-1}, 779–2576 μg kg^{-1}, 1900–4258 μg kg^{-1}, 1247–2562 μg kg^{-1}, 294–1303 μg kg^{-1}, 537–1722 μg kg^{-1} and 1426–2343 μg kg^{-1}, respectively.

The amount of PAHs in the rice husk samples was found twice the amount of rice. Except for rice and water samples, PAHs accumulation was determined in sediment and rice husk samples.

If we summarize briefly, the BghiP and DahA pesticides in the sediment samples in Dam Basin, Meriç-Üyüklütatar Village and the Muhacirkadı-Ergene Basin was be bellowed of limit of detection. It was below the limit of detection of BbF, BkF, BaP, BghiP, DahA and IcdP pesticides content in water samples in the Dam Basin, Meriç-Üyüklütatar Village and the Muhacirkadı-Ergene Basin. It was below the limit of detection the BaP, BghiP and DahA pesticides in the rice and rice husk samples in the Dam Basin, Meriç-Üyüklütatar Village and the Muhacirkadı-Ergene Basin.

When the results were examined, it was determined that the amounts of pesticides were higher in the samples taken near the Ergene river, but the amounts in the edible section were less than in the rice husk. Rice husk has shown a very good adsorbent and reduced the transport of EN and PAHs in of food. EN and PAHs levels in samples taken from river, stream, or near the canal were found to be higher than the samples taken from the inner sides.

4. Conclusion

Ergene River Basin surroundings were selected for this study: one heavily contaminated sites, moderately contaminated sites, and one less contaminated reference sites. The modified QuEChERS method used in this study was practical for mixtures found in environmental samples. This technique performs well, exhibiting good sensitivity, selectivity, and precision in the range of concentrations appropriate for the determination of target analytes. Our study investigated to the Ergene River Basin in sediment, rice, rice husk and water were analyzed for trace organic pollutants. However, the sediment and plant (rice and husk) had measurable and sometimes high levels of PAHs, even though no industrial sources of pollution were known. Other sources of PAH contamination may include runoff from paved roads and exhaust from farm machinery, and factory wastes immediate of the sampling stations. Therefore, in the alives feeding with husk of rice, there may be bioaccumulation of EN and PAHs. Ecological risk assessments for the sediment efficacies concluded that response actions were necessary for the sediment and husk, except for water and rice.

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